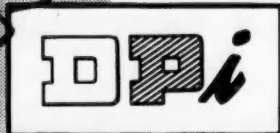


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FLUORESCENT INDICATORS* DEC 11 1957

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The closely similar phenomena of fluorescence and phosphorescence are produced when molecules excited by electromagnetic radiation emit light upon returning to their normal (ground) state. If the emitted light persists after cessation of the exciting radiation, the phenomenon is called "phosphorescence," whereas when radiation ceases immediately upon removal of the exciting source, the phenomenon is termed "fluorescence." In terms of fundamental principles, a more definite distinction can be made. For a theoretical treatment of these subjects, the reader is referred to "Fluorescence and Phosphorescence," by W. West (1).

The use of fluorescent indicators in chemical systems has an exact analog in the use of visual color indicators. The chemical principles involved are basically the same for both visual and fluorescent indicators, the only difference being the physical origin of the colors produced. Thus, only those compounds whose fluorescence in solution is highly sensitive to the solution environment are useful as fluorescent indicators. A good, fluorescent acid-base indicator is one whose fluorescence is highly dependent upon the pH of the solution. In some cases, the wavelength of emitted light changes markedly with pH while, in other cases, the intensity of fluorescence at a given wavelength is related to pH. Kavanagh and Goodwin (2) studied the dependence of the wavelength of fluorescent radiation upon pH and have tabulated curves relating these factors for a number of compounds. Haitinger (3) described the use of quinine and Phosphin 3R as fluorescent indicators and has calibrated both the color and the intensity of fluorescence in the pH range, 2 to 9.5.

By using buffered solutions, Linser (4) studied the intensity of fluorescent radiation as a function of pH for three indicators. He worked with esculin, fluorescein, and umbelliferone and concluded that, with an indicator concentration of 0.00005%, it was possible to determine the pH with an accuracy of about 0.05 pH units. Gotó (5) has also studied the relation of intensity of fluorescence of certain indicators to pH and its dependence upon the concentration of the indicator. Szebellédy and Sik (6) studied the fluorescent characteristics of several common visual indicators and have shown that, whereas visual color changes are imperceptible in highly colored solutions, changes in fluorescent radiation can be detected. Included in the same paper are recommendations for the use of certain fluorescent indicators in solutions of definite color.

Nonaqueous titrations in glacial acetic acid with perchloric acid as a titrant have been carried out by Tomiček (7), using 1-naphthylamine-7-sulfonamide and several

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isomeric and analogous amides as fluorescent indicators.

The pH of solutions containing corrosives, such as hydrofluoric acid, which attack the glass electrode or highly nonpolar solvents which may interfere with the proper functioning of a pH meter, can be measured advantageously by means of fluorescence. Highly colored materials, such as foodstuffs, plant extracts, animal liquors, and essential oils, have been titrated conveniently with fluorescent indicators (8). As an example, umbelliferone has been used in the titration of red wines and the results are in close agreement with those obtained potentiometrically (9).

A simple black box, of cardboard, lined with black paper, containing a source of ultraviolet radiation is all that is needed for comparing fluorescent solutions. Radley and Grant (10) suggested performing the titration with ultraviolet radiation as the sole illuminant. For more precise determinations, the use of a spectrophotometer is desirable.

A large number of compounds have been mentioned in the literature as being useful fluorescent indicators for the determination of pH. Not all observers agree on the color changes involved and the pH range at which the color change occurs. This may be due, at least in part, to differences in concentration and purity of the indicators. Reproducible values have been obtained in these Laboratories on indicators from our own stock representative of the purity now available. In the accompanying table are included products which have been described as useful, a reported color change being recorded in Column II and a reference in Column III. Those marked "EK" in Column III are stock of Eastman Organic Chemicals, for which the color changes and the pH ranges listed were observed in these Laboratories.

Fluorescent indicators are not limited to their use in the determination of pH. Extensive studies have been made on titrations in which sparingly soluble compounds are formed. Del Campo and Sierra (11) used umbelliferone and quinine for titrating tungstate and ferrocyanide with plumbous ion. Gotó (5) has shown that umbelliferone, β -naphthol, and β -naphthoic acid are satisfactory fluorescent adsorption indicators for the titration of silver nitrate with potassium chloride. Kocsis and co-workers (12) have reported that silver ions can be titrated with halide ions using various fluorescent indicators. This may be done in the presence of colored ions, such as Ni^{++} , Co^{+++} , Cu^{++} , and Fe^{+++} by using fluorescein or umbelliferone. Déribéré (13) has described the use of several fluorescent indicators for the titration of certain halide mixtures and thiocyanate in the presence of oxalate.

The use of fluorescence can also be applied to oxidation-reduction systems. In cases where the components of the system themselves fluoresce, the course of an oxidation-reduction reaction can be followed by observing the change in fluorescence of the system under ultraviolet radiation (14). Déribéré (15) has described the use of fluorescent indicators in oxidation-reduction systems.

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Fluorescent Indicators

Indicator	Color Change*	pH Range	Reference*
4-Methylumbelliferone	G-WB	0.0-2.0	EK
3,6-Dihydroxyphthalimide	G-YG	0.0-2.5	7 (Bib.)
Benzoflavin	Y-G	0.3-1.7	7 (Bib.)
Ethoxyacridone	G-B	1.2-3.2	7 (Bib.)
3,6-Tetramethyldiaminoxanthone	G-B	1.2-3.4	7 (Bib.)
Esculin	C-B	1.5-2.0	13 (Ref.)
Eosin Yellowish	C-Y	2.0-3.5	EK
7-Amino-1,3-naphthalenedisulfonic Acid	WB-B	2.0-4.0	EK
1-Hydroxy-2-naphthoic Acid	C-B	2.5-3.5	5 (Ref.)
Salicylic Acid	C-B	2.5-4.0	EK
2',4',5',7'-Tetrabromofluorescein Sodium Salt	C-G	2.5-4.5	5 (Ref.)
2-Naphthylamine	C-V	2.8-4.4	7 (Bib.)
Erythrosin	C-B	3.0-4.0	EK
1-Naphthylamine	C-B	3.0-4.5	EK
3-Hydroxy-2-naphthoic Acid	B-G	3.0-6.8	11 (Bib.)
o-Phenylenediamine	G-C	3.1-4.4	12 (Ref.)
p-Phenylenediamine	C-OY	3.1-4.4	12 (Ref.)
5-Aminosalicylic Acid	C-G	3.1-4.4	12 (Ref.)
o-Methoxybenzaldehyde	C-G	3.1-4.4	12 (Ref.)
Phloxine	C-Y	3.4-5.0	2 (Bib.)

Indicator	Color Change*	pH Range	Reference*
Fluorescein	WG-G	4.0-5.0	EK
Quininic Acid	Y-B	4.0-5.0	13 (Bib.)
4,5-Dihydroxy-2,7-naphthalenedisulfonic Acid Disodium Salt	WB-B	4.0-6.0	EK
2',7'-Dichlorofluorescein	WG-G	4.0-6.0	EK
Resorufin	C-O	4.0-6.0	EK
β -Methyl Esculetin	C-B	4.0-6.2	7 (Bib.)
Acridine	G-B	4.5-6.0	EK
3,6-Dihydroxyxanthone	C-BG	5.4-7.6	7 (Bib.)
3,6-Dihydroxyphthalic Acid	B-G	5.8-8.2	7 (Bib.)
Quinine	B-V	5.9-6.1	11 (Ref.)
5-Amino-2,3-dihydro-1,4-phthalazinedione	B-WB	6.0-7.0	EK
3,6-Dihydroxyphthalonitrile	B-G	6.0-8.0	7 (Bib.)
2-Naphthol-6-sulfonic Acid Sodium Salt	C-B	6.0-8.0	5 (Ref.)
Brilliant Diazo Yellow	C-B	6.5-7.5	13 (Ref.)
Thioflavin	C-G	6.5-7.6	1 (Bib.)
4-Methylumbelliferone	WB-B	6.5-8.0	EK
Umbelliferone	O-B	6.5-8.0	11 (Ref.)
Orcinaurine	C-G	6.5-8.0	8 (Bib.)
2-Naphthol	WB-B	7.0-8.5	EK
2-Naphthol-6,8-disulfonic Acid Dipotassium Salt	WB-B	7.0-8.5	EK
Morin	WG-G	7.0-8.5	EK
1-Naphthol	C-BG	7.0-9.0	EK
2-Naphthol-3,6-disulfonic Acid Disodium Salt	WB-B	7.0-9.0	EK
Harmine	B-Y	7.2-8.9	6 (Bib.)
trans- <i>o</i> -Hydroxycinnamic Acid	C-G	7.2-9.0	7 (Bib.)
1-Naphthol-4-sulfonic Acid Sodium Salt	DB-LB	8.0-9.0	4 (Bib.)
1-Naphthol-2-sulfonic Acid Sodium Salt	DB-LB	8.0-9.0	5 (Ref.)
Coumarin	WG-G	8.0-9.5	EK
Acridine Orange	WYG-Y	8.0-10.0	EK
Naphthol AS	C-YG	8.2-10.3	13 (Ref.)
Ethoxyphenylnaphthastilbazonium Chloride	G-O	9.0-11.0	7 (Bib.)
6,7-Dimethoxyisoquinoline-1-carboxylic acid	Y-B	9.5-11.0	13 (Bib.)
Eosin BN	C-Y	10.5-14.0	15 (Ref.)
1-Naphthylamine	B-WB	12.0-13.0	EK
7-Amino-1,3-naphthalenedisulfonic Acid	B-WO	12.0-13.0	EK
Cotarmine	Y-C	12.0-13.0	5 (Bib.)
β -Naphthionic Acid	B-V	12.0-13.0	5 (Bib.)
4-Amino-1-naphthalenesulfonic Acid	B-G	12.0-14.0	EK

*C = colorless; B = blue; G = green; V = violet; O = orange; Y = yellow; D = dark; L = light; W = weak; Ref. = reference in text; Bib. = from Bibliography.

Note: The subject matter contained in this *Bulletin* is for information only, and none of the statements contained herein should be considered as a recommendation for the manufacture or use of any substance, apparatus, or method in violation of any patents now in force or which may issue in the future.

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